



OPEN Determination of the bioavailability of barley grains for selected elements

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Potentially toxic elements selected elements pose a risk of contamination and intoxication of agricultural soil. Such contamination is closely linked to threats to human health, as the bioavailability of these elements allows their transfer from crops into the food chain. The aim of the study is to assess the bioavailability of selected elements in barley grain in case of possible soil contamination with selected selected elements. The main novelty of the work consists in the evaluation of the mutual correlation of selected elements in the bioavailability of spring barley with respect to different treatments. To determine the selected elements bioavailability, the content of selected selected elements was monitored in soil with the addition of NPK and in soil treated with the addition of Mo, Sr, As, Cd. To evaluate the accessibility of selected elements, or their synergism, we used selected methods of inductive statistics. The α -level of 0.05 was set as the decision rule in all statistical tests. Based on our analysis at the unit change of Mo, Mn in spring barley grain increases by an average of 2.14 mg.kg⁻¹ when grown in strontium-enriched soil. According to our study, barley grain at a unit change of As increases by an average in Mn content by 24.44 mg.kg⁻¹ with the addition of Cd. According to our results, the addition of Mo to the soil caused an average decrease in Zn at the unit change of As by 3.4 mg.kg⁻¹. Likewise, an average increase in Mo of 38.45 mg.kg⁻¹ at the unit change of As (addition of Mo) was confirmed. A negative correlation was confirmed between pairs of elements Mo and Zn without the addition of selected elements. The study confirmed statistically significant differences in the content of selected elements in individual treatments compared to the control NPK sample. At the same time, a positive or negative correlation in the bioavailability of selected selected elements was confirmed.

Keywords Potentially toxic elements, Barley, Bioavailability, Synergism, Statistical tests

Abbreviations

df	Degree of freedom
p	Level
N	Sample size
NPK	Fertilizer

Heavy metals or also risk elements are involved in the contamination and intoxication of agricultural soils in many parts of the world. The term heavy metals or also commonly used term potential present element is understood to mean a group of metals and metalloids with an atomic density higher than 4 g.cm⁻³ or 5 times or more greater than water¹. These elements mainly include lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), iron (Fe), arsenic (As), manganese (Mn) and platinum group elements, which affect the growth, development and survival of organisms². These chemical elements are mostly found dispersed in various forms and in various geological formations³.

Arsenic is one of the most toxic from the potentially toxic elements. The availability and distribution of arsenic in soil result mainly from the climatic and geomorphological characteristics of the area. The arsenic content in

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plants is relatively low even when plants grow on contaminated soils⁴. The representation of different forms of arsenic and their mobility depend on the physical and chemical properties of the soil, the proportion of humus, as well as on microbial activity. Microorganisms use arsenic as a precursor for oxidation, reduction, methylation and demethylation processes. The mobility of arsenic in soil is limited by sorption to clay minerals, organic matter and hydrated iron oxides, to a lesser extent by sorption to hydrated aluminium and manganese oxides and possibly by the formation of secondary minerals. In general, arsenates are less toxic to plants than arsenites. Sodium arsenite causes wilting of plants, which is induced by changes in membrane integrity. Arsenates cause yellowing of leaves^{5,6}.

Cadmium accumulates in the soil, mostly in the top layer. With increasing depth, its concentration decreases. It easily passes into the solution and occurs as a Cd^{2+} cation. Cadmium with humic acids forms complexes that are less stable than the complexes with copper and lead. The cadmium content in the soil is also significantly influenced by soil microorganisms. The most intense accumulation of cadmium is characteristic for root tissues, followed by leaves, stems, fruits, and storage organs. Cadmium has a negative effect on biochemical processes. It induces changes in the permeability of the cell wall, affects photosynthesis, transpiration, and inhibits protein synthesis. The most frequently reported symptoms of cadmium phytotoxicity include leaf chlorosis, browning of root hairs or tips of plant roots, reddish-brown discoloration of leaf veins and the appearance of purple-brown spots on the leaves, in extreme cases drying and leaf fall^{7–9}.

Lead is the most widely used heavy metal and its intake from food, due to the toxicity of lead compounds, is one of the most dangerous. The natural source of lead for plants is its content in the soil, which is conditioned by the geological properties of the subsoil. Lead is accumulated in the topsoil, which contributes to its greater circulation in ecosystems, and thus its danger to humans and animals is significantly increased¹⁰. Phytotoxicity of Pb affects plant growth, reduces germination, disrupts cell division, enzymatic activity, etc¹¹.

Stable isotopes of strontium occur naturally as part of minerals (SrSO_4 , SrCO_3 , sandstones). In limestone rocks containing apatite, in which strontium is possible, its concentration can reach up to 73 g.kg^{-1} . Strontium is a natural growth stimulant and can replace Ca in some plants. However, Sr toxicity can exacerbate the intake of essential nutrients, disrupt enzyme activities, and negatively affect plant health¹².

The main sources of contamination are considered to be various substances used in agriculture itself, such as organomineral and inorganic fertilizers, and excessively dosed pesticides¹³. The accumulation of heavy metals in agricultural soil can result in a deterioration of soil quality and can threaten crop productivity and human health throughout the food chain^{14–16}. The long-term presence of heavy metals in the atmosphere, soil or water can cause bioaccumulation and the potential for biomagnification in food chains, which directly harm ecosystems and health¹⁷. Excessive accumulation of heavy metals in soil raises concerns in agricultural production due to their adverse effects on food safety, marketability, and crop yields as a result of their phytotoxicity¹⁸.

The interaction between different heavy metals and their competition for uptake in cereal crops have emerged as critical factors influencing the status of heavy metal contamination in agricultural ecosystems. Elucidation of these interactions is essential for predicting the behavior of heavy metals in the soil-plant system and for developing effective strategies for eliminating the impacts of heavy metal contamination on plants^{19,20}.

Antagonistic effects can occur, in which the presence of one metal inhibits the uptake or translocation of another metal. For example, the presence of high levels of iron in the soil has been found to reduce the uptake of cadmium and lead by cereals. In such cases, iron competes with cadmium and lead for uptake sites on the root surface, limiting their entry into the plant. While this may reduce the accumulation of toxic metals in the edible parts of the crop, it can also affect the nutrient status of the plant and potentially lead to iron deficiency in the grain²¹. Some heavy metals may exhibit synergistic effects on plant uptake and translocation^{22,23}. Synergism occurs when the presence of one metal increases the uptake or accumulation of another metal in a plant. For example, zinc and cadmium have been found to exhibit an synergistic relationship in certain cereal species. The presence of zinc in the soil can increase the uptake of cadmium by cereals, leading to higher cadmium concentrations in the grains²⁴. This phenomenon may have implications for food safety, as it may result in elevated levels of cadmium in cereals consumed by humans²⁵. These interactions depend on factors such as metal properties, soil properties and cereal species characteristics²⁶.

The aim of the study is to assess the biological availability of above-ground barley biomass in the soil contaminated by selected elements. Biological availability was monitored for the risk elements Mo, Sr, As, and Cd. In addition, the mutual interaction between individual soil treatments with the addition of selected elements and the content of selected risk elements (Mo, Mn, Sr, Cr, As, Cd, Pb, Cu, Zn) in the barley was studied.

The aim of the extended monitoring, i.e., the assessment of a broader spectrum of elements in spring barley biomass, was to evaluate potential interactions (synergistic/antagonistic effects) between the added selected trace elements and the naturally occurring essential or non-essential metals. This enabled us to assess the uptake of other metals (selected elements) present in the soil matrix, which may influence the accumulation and potentially also the toxicity of metals in the plant.

Focusing on the combined monitoring of multiple selected elements in barley after model soil treatment provides new insights into the interactions of absorption of a broader spectrum of elements, allowing the investigation of bioaccumulation patterns of toxic and microbiogenic elements in plants (spring barley) under stress soil contamination.

Materials and methods

Several regions in Slovakia have been identified where elevated levels of heavy metals and potentially toxic elements in soils have been monitored as a result of anthropogenic environmental burdens. This issue has been highlighted in several studies^{27–29}.

One such region is the Upper Nitra area, where risk elements under agroecological conditions were studied by Kulich (1994)³⁰. He pointed out elevated levels of trace elements and microelements in agricultural soils located

within the cadastral areas of Čereňany, Oslany, and Velké Uherce (Table 1), which are within the emission range of the Nováky Power Plant.

The selected doses corresponded with the approximate content of these elements in the soil analysed from the soil samples taken in the vicinity of Elektrárň Nováky, cadastral area of Oslany and Čereňany, and which results are shown in Table 1.

In connection with these findings, we experimentally investigated the impact of these elements on the biomass production of a selected agricultural plant in model vegetation experiments, while also monitoring their accumulation in the economically valuable component (i.e., in the grain) and assessing the interactions in the accumulation of other elements (Mn, Cr, Pb, Cu, Zn) in the grain of spring barley (*Hordeum vulgare*, var. *distichon* L.).

Organization of the experiment

The model vegetation experiment was conducted during the growing season of 2021, starting in April, under the conditions of a vegetation cage without artificial lighting. For the cultivation of the test plant, we used standard Mitscherlich plastic containers with perforated bottoms. The soil for the experiment consisted of the upper humus horizon of modal luvisol (LMm), clayey, with a medium supply of basic acceptable nutrients and a humus content of 2.1%. The agrochemical characteristics of the soil used are provided in Table 2.

The prepared soil was placed into plastic containers, where 6 kg of substrate consisting of soil and silica sand (in a 5:1 ratio) was weighed. Basic nutrients, NPK, were added to this substrate by introducing nitrogen (N) in the form of NH_4NO_3 , phosphorus (P) in the form of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{CaHPO}_4$, and potassium (K) in the form of 40% KCl (ratio 1:1.2:1.4).

The arrangement of the experimental variants and the doses of intoxication solutions (modeling the condition of contaminated soils in the Upper Nitra region) were as follows:

A – variant : NPK – control

B – variant : NPK + solution $(\text{NH}_4)_2\text{MoO}_7$, dose 20 mg Mo.kg⁻¹ of substrate

C – variant : NPK + solution $\text{Sr}(\text{NO}_3)_2$, dose 10 mg Sr.kg⁻¹ of substrate

D – variant : NPK + solution $\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, dose 20 mg As.kg⁻¹ of substrate

E – variant : NPK + solution $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, dose 5 mg Cd.kg⁻¹ of substrate

In the variants with molybdenum and strontium, the dose of NH_4NO_3 was adjusted to account for the presence of nitrogen in the intoxication solution. The intoxication solutions according to the experimental variants were added to the prepared base substrate in each container, in the form of Mo – $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}$, Sr – $\text{Sr}(\text{NO}_3)_2$, As – $\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, and Cd – $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. Distilled water was then added for irrigation to reach the maximum water-holding capacity.

The prepared containers (with numerical labeling) were placed on stands with a catch glass container underneath, arranged such that 5 containers from each variant were placed next to each other. The sowing of the test plant seeds was done after 7 days, at a depth of 20 mm, with 35 seeds per container. After germination (on the 11th day after sowing), thinning was done to maintain the same number of plants in each container (30 plants of the test crop per container). A total of 18 days passed from the addition of the intoxication solutions to the start of plant germination, which is important for the equilibration period. Subsequently, the substrate moisture was maintained at 60% of its maximum water-holding capacity (WHC). During the phenological stage of stem elongation, support stands were added to the containers to prevent the stems from lodging.

In the experiment, we grew:

- Spring barley (*Hordeum vulgare*, var. *distichon* L.), variety Orbit.

Element	Average element content [mg.kg ⁻¹]	Range of element contents [mg.kg ⁻¹]	
		x _{min}	x _{max}
Mo	19.71 ± 11.54	1.48	50.8
Sr	9.55 ± 2.49	5.66	12.80
As	20.14 ± 11.43	1.54	37.88
Cd	4.83 ± 2.46	0.41	10.15

Table 1. Contents of the studied elements in soil samples collected from the surroundings of the Nováky power Plant—extract with 2 M HNO_3 ^{30,31}. Note: in compliance with the Act No. 220/2004 Coll. on the Protection and Use of Agricultural Land, Annexe No. 2, Table 1, the limits are given for the content of As in clay soil (25 mg.kg⁻¹) and for Cd in clay soil (0.7 mg.kg⁻¹). Limit values of risk elements in the relation of agricultural land and plant (so-called critical values) comply with the Annexe No. 2 of the Act No. 220/2004 Coll. on the Protection and Use of Agricultural Land for As (0.4 mg.kg⁻¹) and for Cd (0.1 mg.kg⁻¹).

Indicator	Expressed in units	Value	Comment
Exchange reaction	pH/KCl	6.83 ± 0.13	Determined by electrode in 2 M KCl
Humus content	(%)	2.10 ± 0.09	Measured after 24 h of equilibrium as soil organic carbon content (COX) determined by Tyurin's method modified by Simakov with conversion (1.724) *
Exchangeable phosphorus content	(mg.kg ⁻¹)	56.80 ± 3.52	Extract in Mehlich II. - determined photocolourimetrically
Exchangeable potassium content	(mg.kg ⁻¹)	185.60 ± 11.12	Extract in Mehlich II. - determined photometrically
Mo (releasable)	(mg.kg ⁻¹)	1.3 ± 0.29	Extract in 2 M HNO ₃ - determined by AAS
Sr (releasable)	(mg.kg ⁻¹)	0.92 ± 0.13	Extract in 2 M HNO ₃ - determined by AAS
As (releasable)	(mg.kg ⁻¹)	1.49 ± 0.41	Extract in 2 M HNO ₃ - determined by AAS
Cd (releasable)	(mg.kg ⁻¹)	0.18 ± 0.08	Extract in 2 M HNO ₃ - determined by AAS
Mn (releasable)	(mg.kg ⁻¹)	340.8 ± 11.3	Extract in 2 M HNO ₃ - determined by AAS
Cr (releasable)	(mg.kg ⁻¹)	2.23 ± 0.81	Extract in 2 M HNO ₃ - determined by AAS
Pb (releasable)	(mg.kg ⁻¹)	11.8 ± 1.4	Extract in 2 M HNO ₃ - determined by AAS
Cu (releasable)	(mg.kg ⁻¹)	0.38 ± 0.14	Extract in 2 M HNO ₃ - determined by AAS
Zn (releasable)	(mg.kg ⁻¹)	8.4 ± 1.02	Extract in 2 M HNO ₃ - determined by AAS

Table 2. Agrochemical characteristics of the soil used in the experiment.

The biological material was collected at full physiological maturity in June (the seed moisture was approximately 15–16%) by cutting the plants about 1 cm above the surface of the substrate. The plants were placed on filter paper. The ears were cut at the location of the last internode, and the grains were separated from the ear spindle using tweezers. The weight of the grains was determined on prepared scales. The obtained data were recorded according to the container number and the experimental variant. The grains were used for production evaluation (grain weight, or yield given in grams per container) and chemical analysis.

Analysis of plant material

After collecting the plant material, the material (seeds) was obtained according to the variants and containers (presented in repetitions within the variant), washed with deionized water, and placed in a drying oven set to 60 °C. After drying, the seeds were homogenized in a coarse mill, and subsequently, the material was ground in finer mills for further chemical analysis. To achieve a constant dry weight, plant and soil samples were dried at a temperature of 40 ± 3.0 °C in an electric drying oven. The prepared biological material was then mineralized in a microwave mineralization system.

Homogenized plant material samples were accurately weighed to 1 ± 0.001 g on analytical balances. The sample was mineralized in a mixture of redistilled water (deionized water) and concentrated HNO₃ (per analysis - Merck, Darmstadt, Germany) in a 1:1 ratio. The weighed sample was placed in the mineralization chamber, and 5 ml of deionized water and 5 ml of concentrated nitric acid were added. The chamber was closed, and the sample was mineralized in a microwave digestion apparatus (MARS X-press, CEM, USA). Table 3 shows the course of mineralization – i.e., time and temperature (total time 55 min).

After mineralization, the digests were filtered through quantitative filter paper MUNKTELL grade 390, 84 g.m⁻² (green) into 50 ml volumetric flasks. The flasks were then filled up to exactly 50 ml with deionized water. A blank sample (without plant material) and reference samples were prepared in the same way. Following mineralization, analyses were performed using atomic absorption spectrophotometry (AAS) with the VARIAN AA 240FS instrument (Australia). The obtained numerical data were recalculated to mg.kg⁻¹, and the results from 10 measurements per variant were statistically processed.

Quality control

To evaluate the accuracy and ensure the traceability of the measurement results, certified reference materials (CRM), specifically SRM 1567b, were used, and validation parameters were assessed. The calibration coefficient of the linearity of the calibration curve was calculated. Accuracy values were expressed as the coefficient of variation for all elements. The results of parametric tests comparing mean values confirmed that there were no statistically significant differences between the measured and certified concentrations. Table 4 presents the

Phase	Power (W)	Power (%)	Ramp-up (min)	Temperature (°C)	Hold time (min)
Initialization (achieving specified conditions)	800	90	15	150	10
Mineralization (maintaining specified conditions)	800	90	10	160	15
Cooling	–	–	–	–	20

Table 3. Phases and parameters of the mineralization process.

Elements	Mass fraction (mg.kg ⁻¹)	Limit of detection (LOD) (µg.kg ⁻¹)	Limit of quantitation (LOQ) (µg.kg ⁻¹)	Relative percent difference (RPD) (%)
Mo	0.464 ± 0.034	0.63	2	10
Mn	9.00 ± 0.78	3.2	10	9
Sr	–	–	–	–
Cr	1.14 ± 0.10	1.4	4.3	8
As	0.0048 ± 0.0003	2.1	6.7	11
Cd	0.0254 ± 0.0009	0.79	2.5	7
Pb	0.0104 ± 0.0024	1.1	3.5	8
Cu	2.03 ± 0.14	9.8	31	9
Zn	11.61 ± 0.26	370	1200	11

Table 4. Dry-mass basis for selected Element and limit of detection (LOD) and limit of quantitation (LOQ) in SRM 1567b (NIST 1567b).

dry-mass basis data for selected elements, along with the limits of detection (LOD) and limits of quantification (LOQ) in SRM 1567b (NIST 1567b).

Data collection and assessment

The experiment was completed by harvesting the biomass of cultivated plants at the stage of full physiological maturity. When harvesting, the plants were cut at a height of 1 cm above the surface. From each container, the entire above-ground biomass was placed on a prepared large filter paper marked with the container number and the letter of the variant. In one variant, five repetitions were performed. After collecting biological material, the inflorescence was separated from the stems at the place of the last internode. The weight of grain and straw was determined on the prepared scales. The obtained data were recorded according to the container number and variant.

Statistical data analysis

At the beginning of the statistical analyses, basic descriptive characteristics such as arithmetic mean and standard deviation were calculated for the input data.

Significant differences in the content of potentially toxic elements due to different soil modifications were tested using the Student's two-sample T-test. The null hypothesis of equality of two means ($H_0: \mu_1 = \mu_2$) is tested against the alternative hypothesis of inequality ($H_1: \mu_1 \neq \mu_2$). The test statistic based on the sample data is defined by the following formula (Eq. 1).

$$T = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}} \cdot \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}} \quad (1)$$

and has approximately Student's distribution with $n_1 + n_2 - 2$ degree of freedom. To present interval estimates of mean selected elements content values were used boxplots.

The content of a potentially toxic element depending on the presence of another element was evaluated using a simple regression and correlation analysis. Linear regression function given by the formula describes the dependence of one dependent variable Y on one independent (Eq. 2).

$$y_i = \beta_0 + \beta_1 x_i + \varepsilon_i \quad (2)$$

variable X , where β_0 parameter is intercept, β_1 is regression coefficient (slope), and ε is random error. The significance of the regression coefficient is tested using the t test statistic in the form (Eq. 3).

Variant	Mo		Mn		Sr		Cr		As	
	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.
A	4.13	1.01	28.74	1.06	1.24	0.52	1.47	0.59	0.31	0.06
B	17.34	1.46	29.09	1.16	1.36	0.43	1.12	0.20	0.29	0.02
C	11.89	0.76	28.35	2.25	8.83	1.48	1.34	0.47	0.29	0.04
D	5.01	4.30	26.67	3.42	1.84	0.39	1.43	0.46	2.48	0.41
E	2.67	0.75	26.54	1.37	2.05	0.69	1.47	0.51	0.25	0.04
Variant	Cd		Pb		Cu		Zn		-	
	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.	Mean [mg.kg ⁻¹]	St. dev.	-	-
A	0.41	0.06	0.48	0.13	2.90	0.58	23.20	5.19	-	-
B	0.38	0.05	0.37	0.06	2.19	0.46	24.53	2.77	-	-
C	0.44	0.08	0.37	0.08	2.52	0.42	26.21	2.49	-	-
D	0.33	0.07	0.34	0.07	2.50	0.56	26.44	1.40	-	-
E	4.43	0.73	0.39	0.07	2.36	0.86	23.04	1.59	-	-

Table 5. Decomposition table of descriptive statistics.

Variant	Mo		Sr		As		Cd	
	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF
A	4.13 ± 1.01	3.15	1.24 ± 0.52	1.35	0.31 ± 0.06	0.21	0.41 ± 0.06	2.28
B	17.34 ± 1.46	0.81	1.36 ± 0.43	1.48	0.29 ± 0.02	0.19	0.38 ± 0.05	2.11
C	11.89 ± 0.76	9.15	8.83 ± 1.48	0.81	0.29 ± 0.04	0.19	0.44 ± 0.08	2.44
D	5.01 ± 4.30	3.85	1.84 ± 0.39	2.00	2.48 ± 0.41	0.12	0.33 ± 0.07	1.83
E	2.67 ± 0.75	2.5	2.05 ± 0.69	2.23	0.25 ± 0.04	0.17	4.43 ± 0.73	0.86

Table 6. Contents of mo, sr, as, and cd in the grain of spring barley and bioconcentration factor (BCF).

$$t = \frac{b_1}{s_{b_1}} \quad (3)$$

where b_1 is the sample slope and s_{b_1} its standard deviation. Specifically, the null hypothesis $\beta_1 = 0$ against the alternative hypothesis $\beta_1 \neq 0$ is tested. In case of confirmed significant dependence the regression coefficient is interpreted as the average change in Y per unit change in X . The correlation coefficient r is also calculated and informs about the strength of the observed dependence.

The α -level of 0.05 was set as the decision rule in all statistical tests. Statistical software STATISTICA 12 was used for all statistical analyses. The output tables were subsequently edited for better readability in the MS Excel Office 365.

Results and discussion

Decomposition table of descriptive statistics

Basic data evaluation

In the model experiment, we focused on evaluating the accumulation of selected elements in the grain of spring barley (*Hordeum vulgare* L.), considering that the grain of this crop is a significant food source through which these elements can enter the human food chain. The interactions between the accumulation of specific elements were evaluated depending on the model addition of the element to the soil, which corresponds to the state in real conditions of a contaminated agroecosystem. Therefore, Table 4 presents the contents of the added elements (Mo, Sr, As, and Cd) as well as other significant potentially toxic elements (Mn, Cr, Pb, Cu, and Zn). At the beginning of the statistical data processing, the basic descriptive characteristics presented in Table 5 were calculated from the input data matrix.

When evaluating the added elements (Mo, Sr, As, and Cd), we compared their accumulation not only in the dry matter of the consumable parts of spring barley (*Hordeum vulgare* L.) – i.e., the grain – but also with their contents in the soil. The reported content represents their available contents (leachate in 2 M HNO₃) in relatively clean soil and the concentration after addition (i.e., the addition + available content in the soil). The bioconcentration factor was then calculated as the ratio between the content of selected elements in the grain and its acceptable content in the soil. The results are summarized in Table 6.

The basic data suggest that after the addition, all elements (Mo, Sr, As, Cd) significantly increased compared to the control, i.e., the non-contaminated variant. For Mo, the highest content was found in the B-variant (i.e., after its addition) and subsequently in the E, A, D, and C variants. In the E and D variants, it can be stated that the

contents of this element in the grain of spring barley are comparable to those in the non-contaminated A-variant. The exception is the C-variant, where a significantly increased content of this element was also recorded. In the case of Sr concentration in the grain of spring barley, the highest content was observed in the C-variant (i.e., after its addition), while in the other variants, the strontium content was comparable, with a slight increase compared to the control variant. Similarly, for As, the highest content was recorded in variant D (after its model addition), and in the other variants, the contents were approximately at the level of the non-contaminated variant. A similar situation was observed for Cd, where the highest content of this element in the grain of spring barley was found in the E-variant (after its addition), and in the other variants, the contents oscillated at a similar level to the control A-variant.

The bioconcentration factor (BCF) was highest in the control A-variant (non-contaminated soil) for Mo (3.15), followed by Cd (2.28), Sr (1.35), and lowest for As (0.21). In connection with the simulated addition of these elements, the BCF in the grain, despite their increased content, decreased in the following order: Cd (0.86), Mo (0.81), Sr (0.81), and As (0.12).

In addition to evaluating the contents of the model elements added, we also focused on assessing the accumulation of other potentially toxic elements, such as Mn, Cr, Pb, Cu, and Zn. In Table 7, we compare their contents and bioconcentration factors (BCF) in the model experiment.

The results for all elements (Mn, Cr, Pb, Cu, and Zn) indicate that their contents in the grain of spring barley are within comparable ranges in all model variants (B-E) as in the control (non-contaminated) A-variant. The bioconcentration factors for these elements range from Pb (0.04), Mn (0.08–0.09), Cr (0.5–0.66), Cu (2.19–2.9), and Zn (2.74–3.15). A BCF value greater than 1 was recorded only for Cu and Zn. Therefore, we evaluated the mutual correlations between the elements based on statistical analyses.

Evaluation of statistically significant differences of the variants

Average selected elements depending on the variants

Comparison of individual modifications is important for understanding the chemistry of individual PTE behaviour from the viewpoint of their bioavailability for the barley grains. During the evaluation, individual selected elements were compared regarding the soil modification A – NPK; B – Mo; C – Sr; D – As; E – Cd. In Figs. 1, 2, 3, 4, 5, 6, 7, 8 and 9, there are graphically presented 95% confidence intervals of average concentrations of potentially toxic elements. The reference variant was the average concentration of the individual PTE in variant A (addition of NPK – without an addition of selected elements), which was compared to other 4 variants.

To determine the parameters for assessing the statistical significance of the differences in the averages, the T-test (Tables 8, 9, 10, 11, 12, 13, 14, 15 and 16) was used. Significant differences, at the used 5% test significance level, are highlighted in bold in the table. Figures 1, 2, 3, 4, 5, 6, 7, 8 and 9 present 95% confidence intervals for the average content of selected elements for different variants.

When testing the impact assessment of variants B – E compared to the reference variant A (A – NPK; B – Mo; C – Sr; D – As; E – Cd) for the contents of selected elements (Mo, Mn, Sr, Cr, As, Cd, Pb, Cu, and Zn) in barley grains, 5% level of significance of the test was used. In some cases, a less significant dependence is also described, namely at the 10% level of significance of the test.

The effect of different variants on molybdenum content was evaluated as the first one. In the assessment of statistical significance, statistically significant differences were recorded between variants A – B ($p=0.000$), A – C (0%), A – E ($p=0.002$). From the above-mentioned, it can be concluded that the addition of Mo (variant B) and Sr (variant C) led to a statistically significant increase in the molybdenum content in barley grains compared to soil modification with the addition of NPK (without the addition of other selected elements). On the contrary, with the addition of Cd, a significant reduction in the molybdenum content in barley grains was noted compared to soil modification without the addition of selected elements (variant A – NPK). The finding that molybdenum treatment highly increased the bioconcentration of Cd at the reproductive stage compared to the vegetative stage in plants grown in soil contaminated with 50 ppm Cd³² does not correlate with this study. In a comparative study, the research was carried out on hemp. Conversely, according to a study³³ the supply of molybdenum mitigates the cadmium toxicity in fragrant rice by modulating oxidation stress and expressing antioxidant genes. Han et al. focused on research³⁴ on the beneficial effect of molybdenum (Mo) application on rapeseed (*Brassica napus* L.), grown in cadmium-contaminated soil (Cd). Based on the results, exogenous Mo can effectively reduce the toxicity of Cd to rapeseed, and the optimal concentration of Mo was 100 mg/kg under experimental conditions.

When evaluating the manganese content, a statistically significant difference was found out among variants A – E. The addition of Cd caused a statistically significant decrease in the content of Mn (variant E) compared to soil modification without the addition of selected elements (variant A). The addition of As resulted in a

Variant	Mn		Cr		Pb		Cu		Zn	
	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF	Grain (mg.kg ⁻¹)	BCF
A	28.74 ± 1.06	0.08	1.47 ± 0.59	0.66	0.48 ± 0.13	0.04	2.90 ± 0.28	2.9	23.20 ± 5.19	2.76
B	29.09 ± 1.16	0.09	1.12 ± 0.20	0.50	0.37 ± 0.06	0.04	2.19 ± 0.46	2.19	24.53 ± 2.77	2.92
C	28.35 ± 2.25	0.08	1.34 ± 0.47	0.60	0.37 ± 0.08	0.04	2.52 ± 0.42	2.52	26.21 ± 2.49	3.12
D	26.67 ± 3.42	0.08	1.43 ± 0.46	0.64	0.34 ± 0.07	0.04	2.50 ± 0.56	2.5	26.44 ± 1.40	3.15
E	26.54 ± 1.37	0.08	1.47 ± 0.51	0.66	0.39 ± 0.07	0.04	2.36 ± 0.86	2.36	23.04 ± 1.59	2.74

Table 7. Contents of mn, cr, pb, cu, and Zn in the grain of spring barley and in the experimental soil.

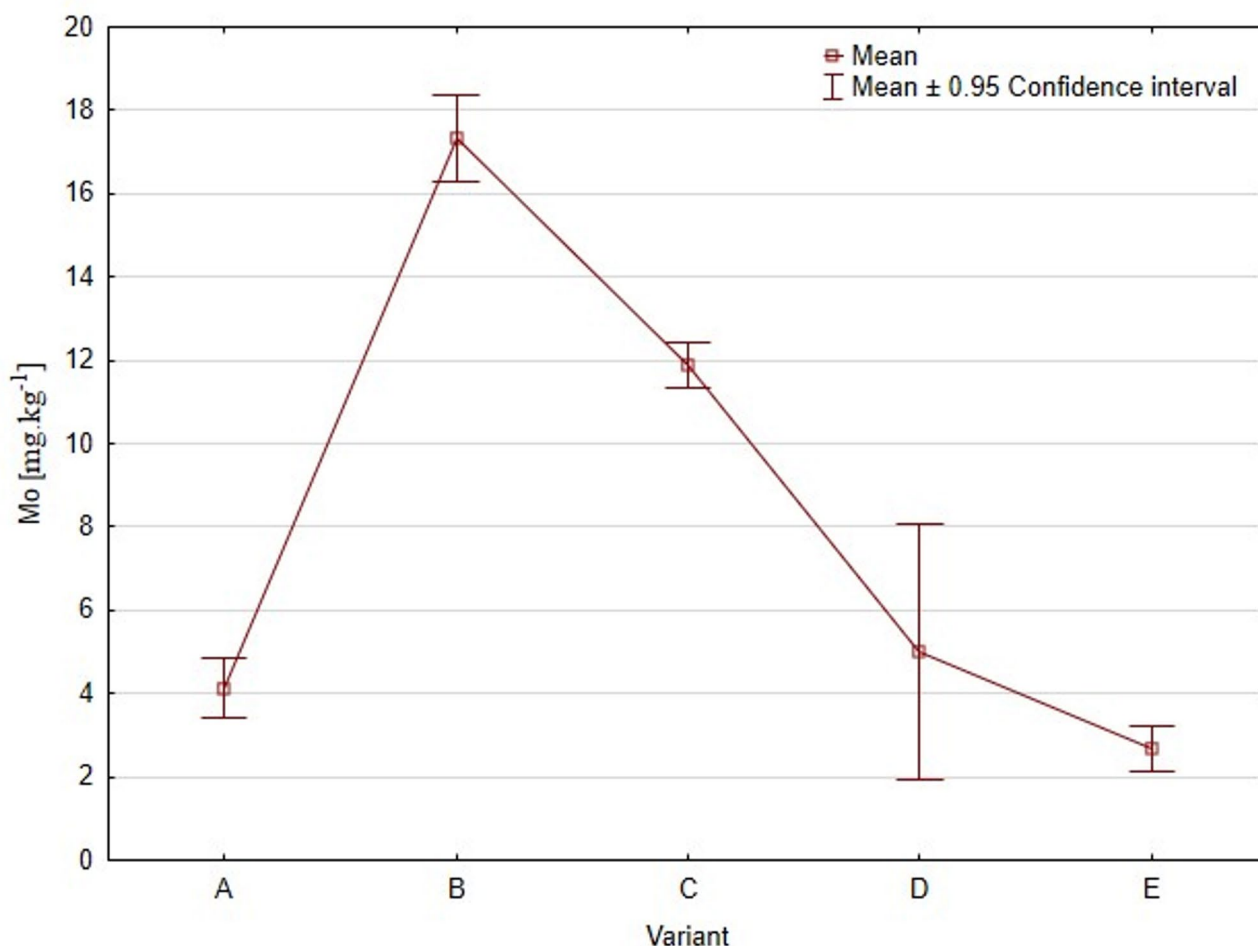


Fig. 1. Average content of Mo in dependence on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

statistically significant reduction in the average concentration of manganese content at the 10% significance level of the test ($p=0.084$). In the past, a study³⁵ focused on the interaction of cadmium and four microelements for uptake and translocation in different barley genotypes was carried out. According to this study, the addition of cadmium reduced the concentration of Mn in grains, roots, and shoots. A significantly negative correlation was found out between the concentration of Mn and the concentration of Cd in different plant organs, suggesting the possibility of mitigating the accumulation of Cd in barley plants by applying these microelements to soils contaminated with Cd. Another study was oriented to differences in yield components and Cd accumulation in the core in response to Cd toxicity in four barley genotypes³⁶. According to the results of this study, a significantly negative correlation was found out between the concentration of Mn and Cd in grains.

By comparing the differences in strontium content among the variants without the addition of selected elements and the variants with additives, 3 statistically significant differences were found out. In the first case, it is an understandable increase in the content of Sr by the addition of this selected elements (variant – C). In the second and third cases, there is an increase in strontium in barley grains by adding As and Cd to the soil. In the past, a study was conducted³⁷ to investigate the combined effect of phosphorus (P) and arsenic (As) applied in soil on P, As, potassium (K), calcium (Ca), magnesium (Mg), silicon (Si), iron (Fe), concentration of manganese (Mn), zinc (Zn), copper (Cu), titanium (Ti), rubidium (Rb), strontium (Sr), barium (Ba), lanthanum (La), and cerium (Ce) in sunflower plants. According to this study, the toxicity of arsenic reduced the concentrations of Sr. A study conducted in the past was focused on the dynamic accumulation, remobilisation and redistribution of Cd in evolving ears of barley³⁸. According to this study, Sr level was increased significantly in stems treated by 2 and 8 μM Cd (19, 3 and 26.2%). Conversely, in another study³⁹ aimed at the problem of Cd contamination in rice, it was found out that strontium mitigated the growth inhibition and toxicity caused by cadmium in rice seeds. The opposite effect of the correlation of these two selected elements was possibly associated with the different physiological behaviour of rice compared to barley.

When monitoring the chromium content and comparing variant A with other variants, a statistically significant difference in Cr concentrations was found out only in the case of the pair of variants A-B. In the study, a reduced concentration of Mo was determined at the addition of 100 mg.kg^{-1} Cr in bean leaves compared to control⁴⁰.

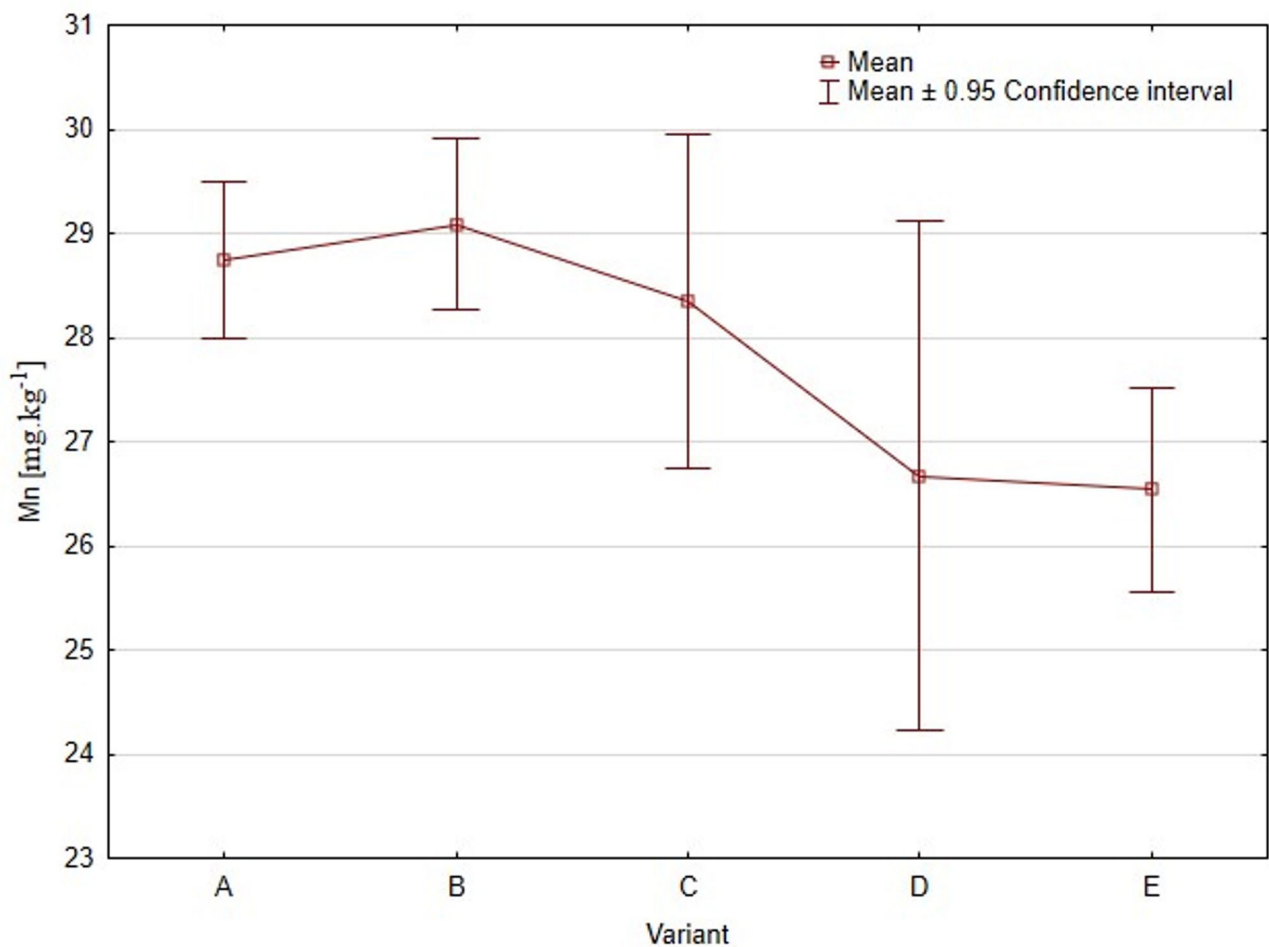


Fig. 2. Average content of Mn depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

Differences in average As concentrations between variant A and the remaining variants were observed in two cases. In the first case, it is an understandable increase due to the addition of As (comparison of variants A – D). In the second case, on the other hand, it is a reduction in the average concentration of As by the addition of Cd compared to NPK soil modification (without the addition of selected elements – variant A). Based on the carried out study, it was found out that growing a rice cultivar with a low Cd content can reduce the As content of rice grains⁴¹.

When monitoring the cadmium content, 2 statistically significant differences in the average concentration between variant A and the remaining variants were noted. One of the cases was the addition of Cd (variants A – E). A statistically significant reduction in cadmium concentration was caused by the addition of arsenic in variant D.

When evaluating the concentration of Pb in barley grains, statistically significant differences in average concentrations were found out among variant A and variants B, C, and D. When comparing variants A and E, statistically significant differences in average concentrations of Pb were observed at the significance level of 10%. In all cases (with the addition of Mo, Sr, As, and Cd), an antagonistic effect on Pb concentration was observed compared to the control. McBride in their study⁴² assessed the effectiveness of soil modifications to reduce the transfer of Pb and As to leafy green vegetables from historically contaminated soils. A low degree of correlation between Pb and As intake from soil contaminated with both selected elements was found out in their study. Liu et al. focused on studying cultivar variation in the accumulation and distribution of cadmium and lead among 30 wheat cultivars (*Triticum aestivum* L.)⁴³. Based on this study, an antagonistic interaction between Cd and Pb in accumulation in wheat roots and shoots was confirmed, which will be further studied in field experiments.

By evaluating the average copper concentrations in individual variants, only one case of differences in the level of statistical significance was found. The addition of Mo caused a statistically significant decrease in the average concentration of Cu in barley grains. Shi et al. conducted a potted culture experiment to study the effects of *Claroideoglomus etunicatum* BEG 168 vaccination on growth and Mo content in maize growing in soil supplemented with different levels (0; 1,000; 2,000; 4,000 mg.kg⁻¹)⁴⁴. Based on this study, the addition of Mo reduced the dry weight of the plants and the content of leaf pigment, as well as the intake of Cu in shoots and roots.

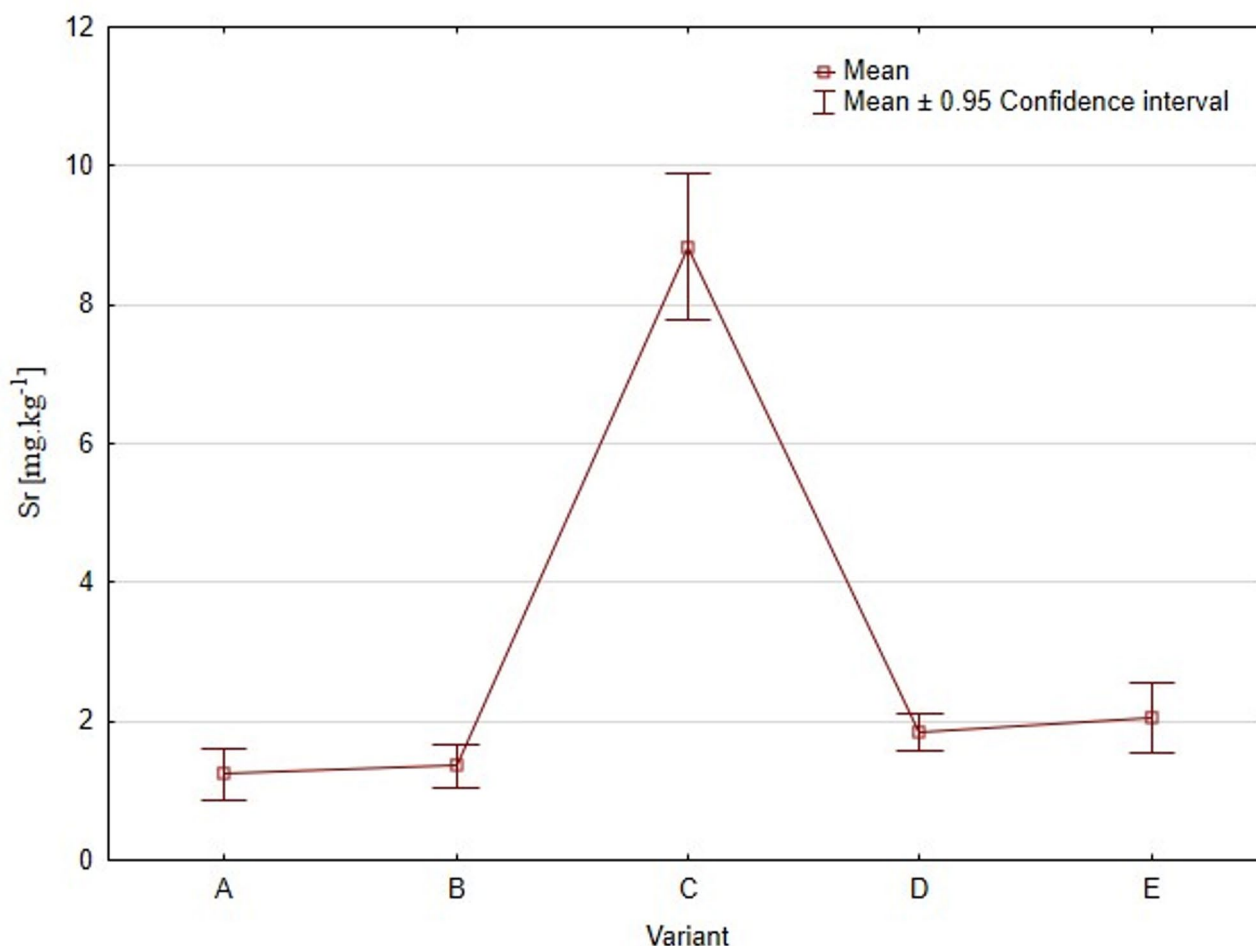


Fig. 3. Average content of Sr depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

The last monitored selected elements was zinc. A statistically significant difference in the average concentration of this selected elements was monitored when comparing variant A with variant D. Soil modification with the addition of As caused a statistically significant increase in the average concentration of Zn. According to a previous study³⁷ the toxicity of arsenic reduced the concentrations of Zn.

Correlation of a pair of selected elements

In Table 17, there is an overview of significant ($\alpha=5\%$) dependences between the pairs of selected elements. Values of regression coefficients (slope) inform about the average change of element Y to the unit change of element X.

Average selected elements depending on the variants

When testing the impact assessment of variants B – E compared to the reference variant A (A – NPK; B – Mo; C – Sr; D – As; E – Cd) for the contents of selected elements (Mo, Mn, Sr, Cr, As, Cd, Pb, Cu, and Zn) in barley grains, 5% level of significance of the test was used. In some cases, a less significant dependence is also described, namely at the 10% level of significance of the test.

The effect of different variants on molybdenum content was evaluated as the first one.

This element is a significant microbiogenic component with an indispensable function in the nitrogen metabolism within the soil-plant system⁴⁵. The importance of molybdenum and its diverse role in plant physiology has recently been the subject of study⁴⁶. However, elevated concentrations of molybdenum can have negative effects on the growth and development of spring wheat (*Triticum aestivum* L.), which manifests in reduced yield as well as increased accumulation^{47,48}.

In the assessment of statistical significance, statistically significant differences were recorded between variants A – B ($p=0.000$), A – C (0%), A – E ($p=0.002$). From the above-mentioned, it can be concluded that the addition of Mo (variant B) and Sr (variant C) led to a statistically significant increase in the molybdenum content in barley grains compared to soil modification with the addition of NPK (without the addition of other selected elements). On the contrary, with the addition of Cd, a significant reduction in the molybdenum content in barley grains was noted compared to soil modification without the addition of selected elements (variant A – NPK). The finding

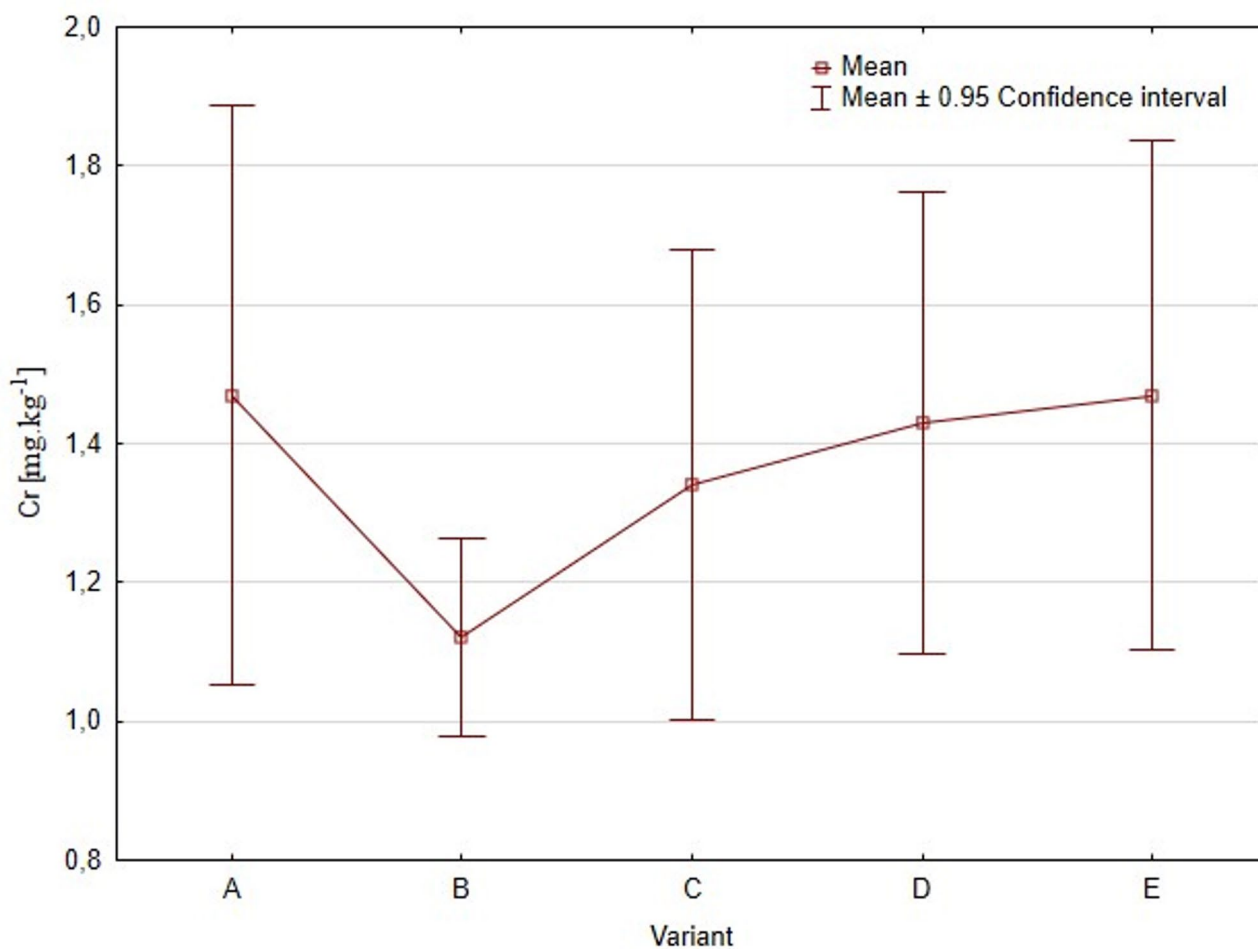


Fig. 4. Average content of Cr depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

that molybdenum treatment highly increased the bioconcentration of Cd at the reproductive stage compared to the vegetative stage in plants grown in soil contaminated with 50 ppm Cd³² does not correlate with this study. In a comparative study, the research was carried out on hemp. Conversely, according to a study³³ the supply of molybdenum mitigates the cadmium toxicity in fragrant rice by modulating oxidation stress and expressing antioxidant genes. Han et al. focused on research³⁴ on the beneficial effect of molybdenum (Mo) application on rapeseed (*Brassica napus* L.), grown in cadmium-contaminated soil (Cd). Based on the results, exogenous Mo can effectively reduce the toxicity of Cd to rapeseed, and the optimal concentration of Mo was 100 mg/kg under experimental conditions.

Another evaluated element was manganese, which is also classified as a micronutrient¹⁷. When evaluating the manganese content, a statistically significant difference was found out among variants A – E. The addition of Cd caused a statistically significant decrease in the content of Mn (variant E) compared to soil modification without the addition of selected elements (variant A). The addition of As resulted in a statistically significant reduction in the average concentration of manganese content at the 10% significance level of the test ($p=0.084$). In the past, a study³⁵ focused on the interaction of cadmium and four microelements for uptake and translocation in different barley genotypes was carried out. According to this study, the addition of cadmium reduced the concentration of Mn in grains, roots, and shoots. A significantly negative correlation was found out between the concentration of Mn and the concentration of Cd in different plant organs, suggesting the possibility of mitigating the accumulation of Cd in barley plants by applying these microelements to soils contaminated with Cd. Another study was oriented to differences in yield components and Cd accumulation in the core in response to Cd toxicity in four barley genotypes³⁶. According to the results of this study, a significantly negative correlation was found out between the concentration of Mn and Cd in grains.

The issue of Mn accumulation in the dry matter of spring barley has also been addressed by Haddad, M., Nassar, D., and Shtaya, M⁴⁹. Their results indicate that the concentrations of iron (Fe) and manganese (Mn) were higher in the control group compared to all spring barley (*Hordeum vulgare* L.) plants treated with metals. The bioconcentration factor (BCF) of Mn in the shoots of this plant was -3.75 , comparable to Cu and Zn, which had BCF values of -3.48 and -3.38 respectively, but lower than that of Cd, which reached -8.24 ⁴⁹. The BCFs calculated by these authors for Mn, Cu, Zn, and Cd were higher than those in our calculations. This discrepancy

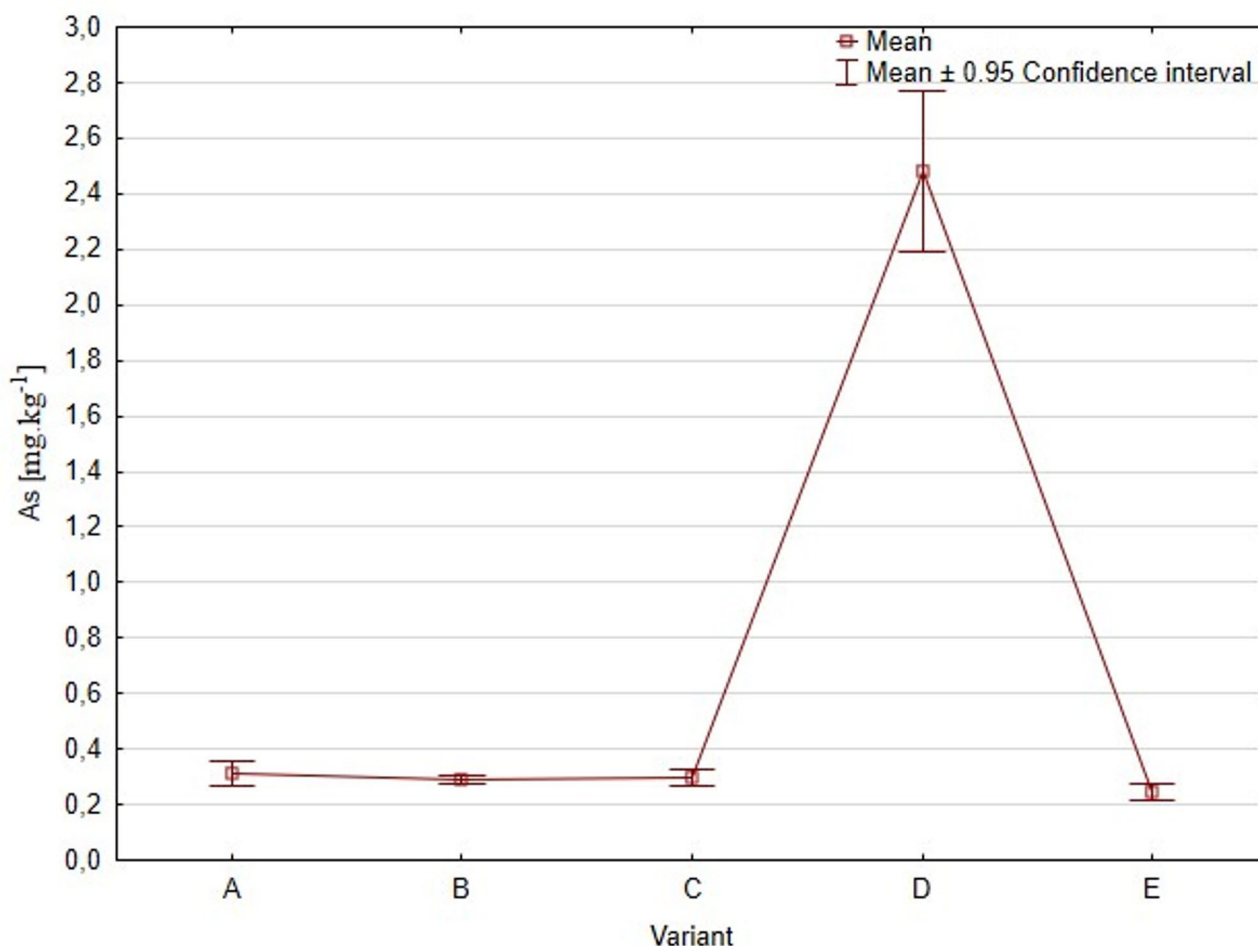


Fig. 5. Average content of As depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

is likely due to the fact that Haddad et al. (2023) based their calculations not only on the elemental content in the aerial (vegetative) parts of the spring barley but also considered the total content of the element in the soil. These authors also calculated the translocation factor (TF), defined as the ratio of element content in the roots to that in the shoots of spring barley (Haddad, M., Nassar, D., & Shtaya, M., 2023). Since our experiment focused solely on the accumulation of elements in the grain, i.e., the generative organ of the plant which is most commonly consumed by humans and livestock, we did not calculate the translocation factor (TF).

Among the potentially toxic elements, strontium (Sr) can also be included, as it is generally considered an indicator of radioactive contamination¹². However, this element is also a component of lignite coal, which was burned at the Nováky power plant from the 1960s to the late 1980s. The issue of Sr in plants and its mobility within the soil–plant system has been addressed by Gupta and Walther⁵⁰ as well as by Laila Salem⁵¹.

By comparing the differences in strontium content among the variants without the addition of selected elements and the variants with additives, 3 statistically significant differences were found out. In the first case, it is an understandable increase in the content of Sr by the addition of this selected elements (variant – C). In the second and third cases, there is an increase in strontium in barley grains by adding As and Cd to the soil. In the past, a study was conducted³⁷ to investigate the combined effect of phosphorus (P) and arsenic (As) applied in soil on P, As, potassium (K), calcium (Ca), magnesium (Mg), silicon (Si), iron (Fe), concentration of manganese (Mn), zinc (Zn), copper (Cu), titanium (Ti), rubidium (Rb), strontium (Sr), barium (Ba), lanthanum (La), and cerium (Ce) in sunflower plants. According to this study, the toxicity of arsenic reduced the concentrations of Sr. A study conducted in the past was focused on the dynamic accumulation, remobilisation and redistribution of Cd in evolving ears of barley³⁸. According to this study, Sr level was increased significantly in stems treated by 2 and 8 μM Cd (19, 3 and 26.2%). Conversely, in another study³⁹ aimed at the problem of Cd contamination in rice, it was found out that strontium mitigated the growth inhibition and toxicity caused by cadmium in rice seeds. The opposite effect of the correlation of these two selected elements was possibly associated with the different physiological behaviour of rice compared to barley.

The interaction between strontium and other trace elements accumulated in the biomass of amaranth (*Amaranthus* spp. L.) was also investigated by Chu et al.⁵². In their study, 33 different varieties of *Amaranthus* were used, and the concentrations of 23 mineral elements in shoots cultivated in fields in Fukushima Prefecture

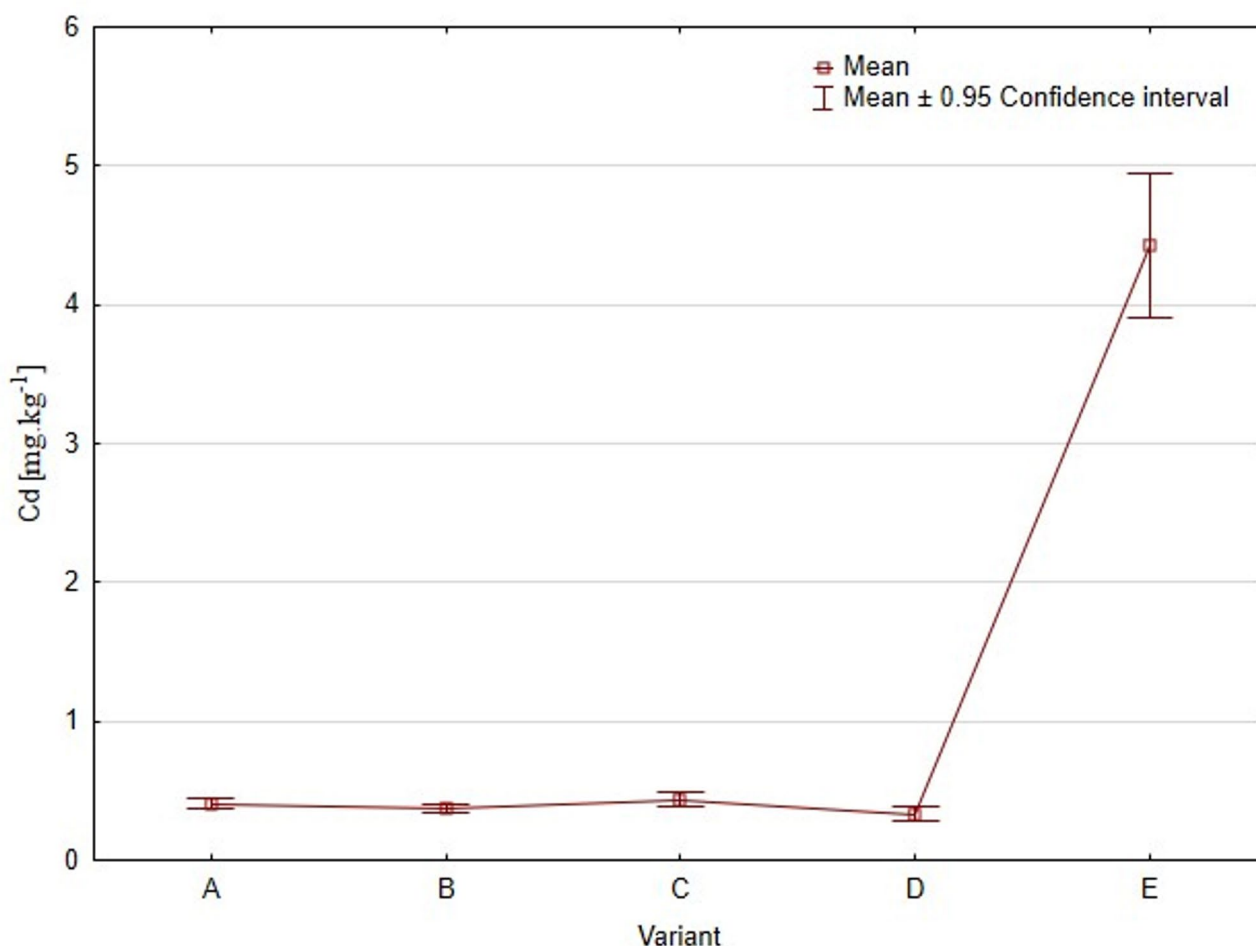


Fig. 6. Average content of Cd depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

were analyzed. Chu et al. (2015) did not find any correlation between the Sr–Cd or Sr–As pairs. This finding could be influenced by species and varietal differences in the uptake of these elements — on one hand by spring barley and on the other by various varieties of *Amaranthus* spp. L.⁵²

From an environmental perspective, chromium (Cr) is an important element that has been monitored in various studies. Soil contaminated with heavy metals, mainly lead (Pb), cadmium (Cd), and chromium (Cr), represents an increasingly alarming environmental problem worldwide⁵³. For example, Kicińska and Wikar⁵⁴ studied the effect of fertilization of soils degraded by the metallurgical industry on the elemental content in lettuce (*Lactuca sativa* L.), where they also reported the accumulation of Cr and Mn. Recently, the transformation of chromium within the contaminated water–soil–plant–animal system has been addressed by Kanwal et al.¹⁵.

When monitoring the chromium content and comparing variant A with other variants, a statistically significant difference in Cr concentrations was found out only in the case of the pair of variants A–B. In the study, a reduced concentration of Mo was determined at the addition of 100 mg.kg⁻¹ Cr in bean leaves compared to control⁴⁰.

A higher concentration of chromium (Cr) in the vegetative parts of spring barley (*Hordeum vulgare* L.), which showed an increasing trend with the elevated application of metals in irrigation water, was also reported by Haddad, M., Nassar, D., and Shtaya, M⁴⁹. In our simulated experiment, the addition of this element similarly resulted in increased accumulation of Cr in the grain of spring barley (*Hordeum vulgare* L.). The accumulation of chromium in maize (*Zea mays* L.) shoots, in connection with the evaluation of heavy metal immobilization through the addition of biochar and compost, was studied by Irfan et al.⁵³. The addition of Pb, Cd, and Cr led to increased concentrations of these elements in the plants; however, the authors also concluded that both biochar and compost reduced the bioavailability of these heavy metals, thereby decreasing their toxicity to the plants. Similar to our methodology, they used a pot experiment, though the effects of heavy metals on production and bioconcentration were assessed in a different plant species. Their experimental soil was enriched not only with Cr but also with Pb and Cd, specifically at concentrations of Pb – 20 mg.kg⁻¹, Cd – 10 mg.kg⁻¹, and Cr – 20 mg.kg⁻¹. In our experiment, only cadmium was applied, and at a lower concentration of 5 mg.kg⁻¹, which limits the possibility of a direct comparison of results. However, a noteworthy aspect of the study by Irfan et al. (2021) is that, in addition to analyzing the element content in the soil prior to the experiment and in the green

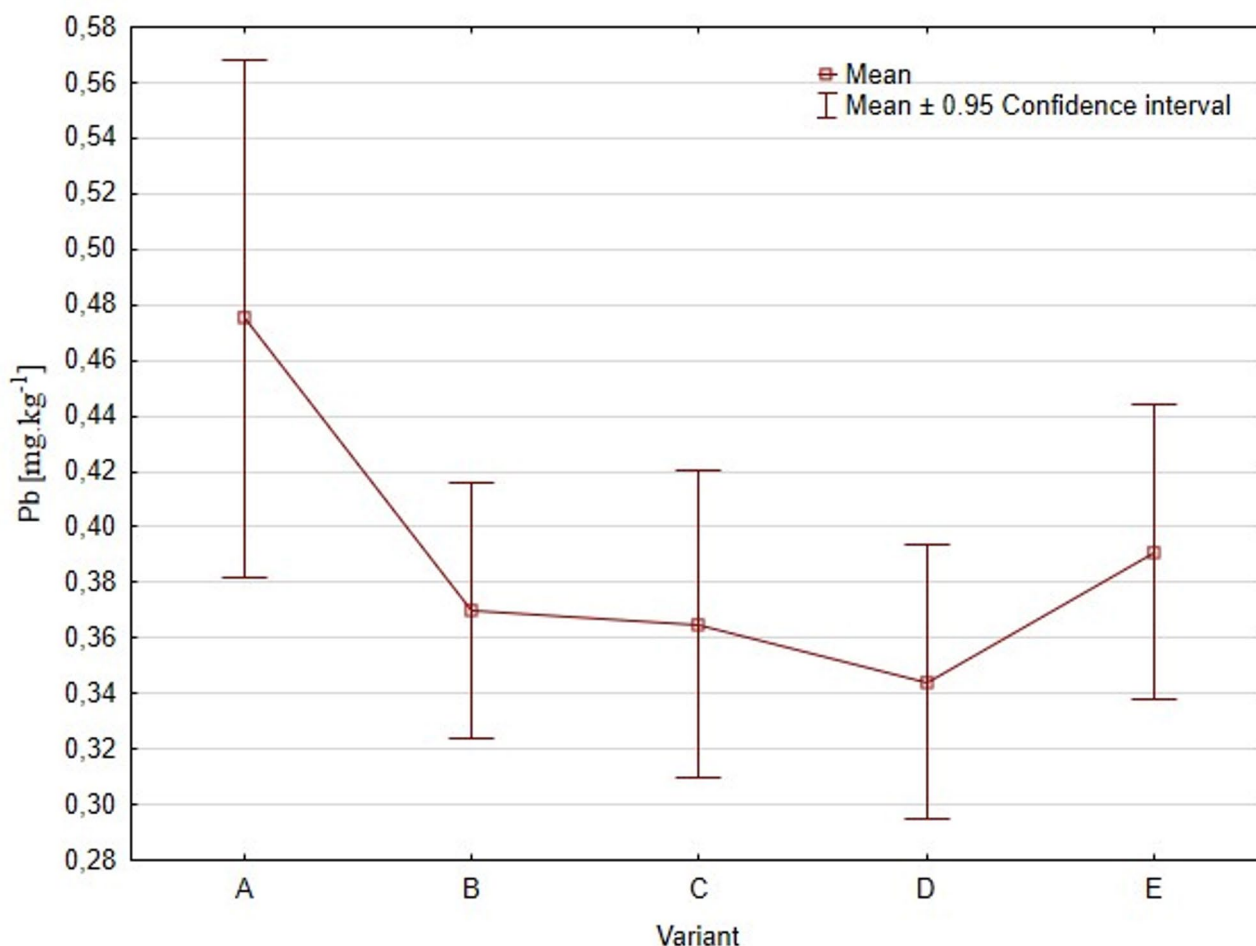


Fig. 7. Average content of Pb depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

parts of the plants, they also evaluated the post-experiment soil composition—presumably to assess changes resulting from the application of varying amounts of biochar and compost. It can nonetheless be stated that the concentrations of Cr, as well as Pb and Cd, reported in their study are generally within the range of our analytical results.

In environmental chemistry, arsenic (As) is considered an element with a high degree of negative effects on living organisms, including plants. It often enters the environment from industrial activities and wastewater discharges⁵⁵ as well as from the combustion of low-quality lignite coal, which, as previously mentioned, was also used at the power plant in Nováky. Therefore, arsenic is regarded as a toxic or potentially toxic element. Differences in average As concentrations between variant A and the other treatments were recorded in two cases. In the first case, a logical increase was observed due to the addition of As (comparison of variants A and D). In the second case, a decrease in the average As concentration was observed following the addition of Cd, compared to the treatment with only basic soil fertilization (i.e., without the addition of potentially toxic elements – variant A).

According to a study by Ishikawa et al.⁴¹ cultivation of rice cultivars with low Cd accumulation can lead to reduced As content in rice grains. A positive correlation between As and Zn was identified in the study by Cheng et al.⁵⁶ in which nine genotypes of rice (*Oryza sativa* L.) were examined. In contrast, a strong positive correlation between As and Cr in rice was reported by Ullah et al.⁵⁷ while a negative correlation between As and Cu was confirmed by Liu et al.⁵⁸ The differences observed in the degree of accumulation and the interactions among these elements are likely influenced not only by their presence and concentrations in the soil but also by different physiological mechanisms of element uptake and storage in the dry biomass of rice and spring barley. Additionally, various ecological and environmental factors may also play a role.

Many studies highlight the health and environmental risks associated with cadmium. Ecological risks stemming from exposure to potentially toxic elements (selected elements) accumulated in soils, including cadmium toxicity, are emphasized by Agyeman et al.⁵⁹ The aim of their study was to create digitized soil maps identifying the health risks posed by selected elements (i.e., lead, arsenic, chromium, nickel, manganese, cadmium, copper, and zinc) to humans. In agricultural soils of the Frýdek-Místek District (Czech Republic), cadmium concentrations ranged from 0.61 to 7.28 mg.kg⁻¹, which to some extent corresponds with our

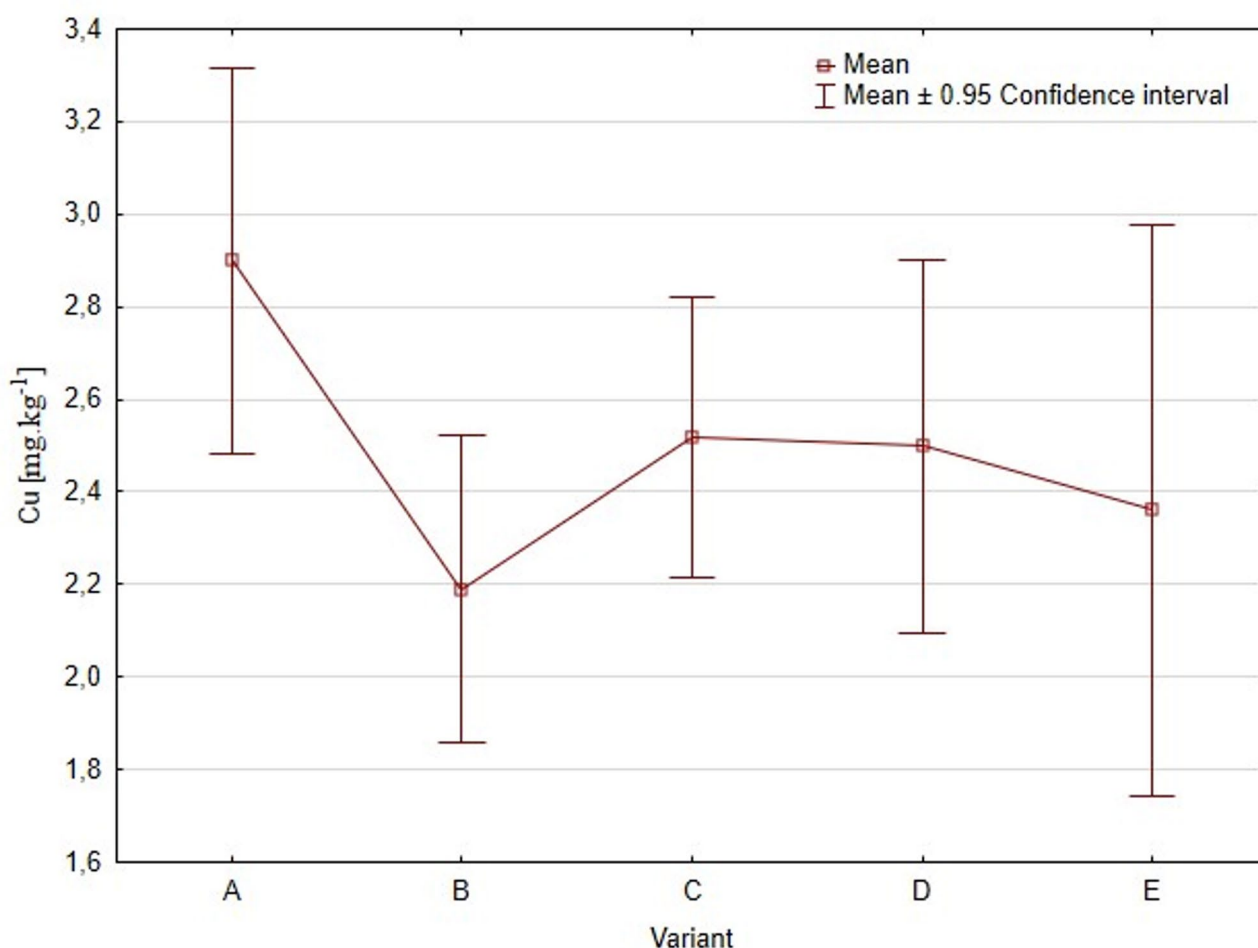


Fig. 8. Average content of Cu depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

findings⁵⁹. Therefore, the cadmium dosage used in our experiment to simulate its effect on accumulation in spring barley (*Hordeum vulgare* L.) grain can be considered a significant environmental risk.

In monitoring cadmium content, two statistically significant differences in mean concentration were observed between variant A and the other treatments. One such case was the direct addition of Cd (at a concentration of 5 mg.kg⁻¹ of experimental soil), which confirms the potential health hazard, as spring barley grain is used for feeding livestock or directly in food production. A slight increase in cadmium concentration compared to the uncontaminated variant A was also caused by the addition of strontium in variant E.

Cadmium accumulation in the vegetative parts and roots of spring barley (*Hordeum vulgare* L.) was also noted by Haddad et al.⁴⁹ who reported concentrations ranging from 0.54 to 0.95 mg.kg⁻¹ in the vegetative parts and 0.03–0.73 mg.kg⁻¹ in the roots. In the variants of our experiment without the addition of this element (i.e., variants A, B, C, and D), the average cadmium content in the grain ranged from 0.33 to 0.44 mg.kg⁻¹, which is comparable to their findings. Only the simulated addition of cadmium resulted in a notable increase in its accumulation.

When monitoring the cadmium content, 2 statistically significant differences in the average concentration between variant A and the remaining variants were noted. One of the cases was the addition of Cd (variants A – E). A statistically significant reduction in cadmium concentration was caused by the addition of arsenic in variant D.

Cadmium is among the most significant heavy metals, and many authors classify it as an element with hyperaccumulation potential⁶⁰. The accumulation of heavy metals, including cadmium, in plants such as *Plantago lanceolata* L., *Lolium multiflorum* L., *Amaranthus retroflexus* L., *Althea rosa* L., and others was studied by Cakaj et al.⁶¹ who also reported increased accumulation of this element in the aerial parts of plants and high BCF values (particularly in species like *Plantago lanceolata* and *Althea rosa* L., up to 8.51 and 6.94, respectively). Compared to our results, these are higher values, which may be attributed to the fact that their data were obtained from experiments using autochthonous species, the method of BCF calculation (the ratio of content in aerial plant parts to total element content in soil), and the fact that our observations focused on accumulation in generative organs (grain).

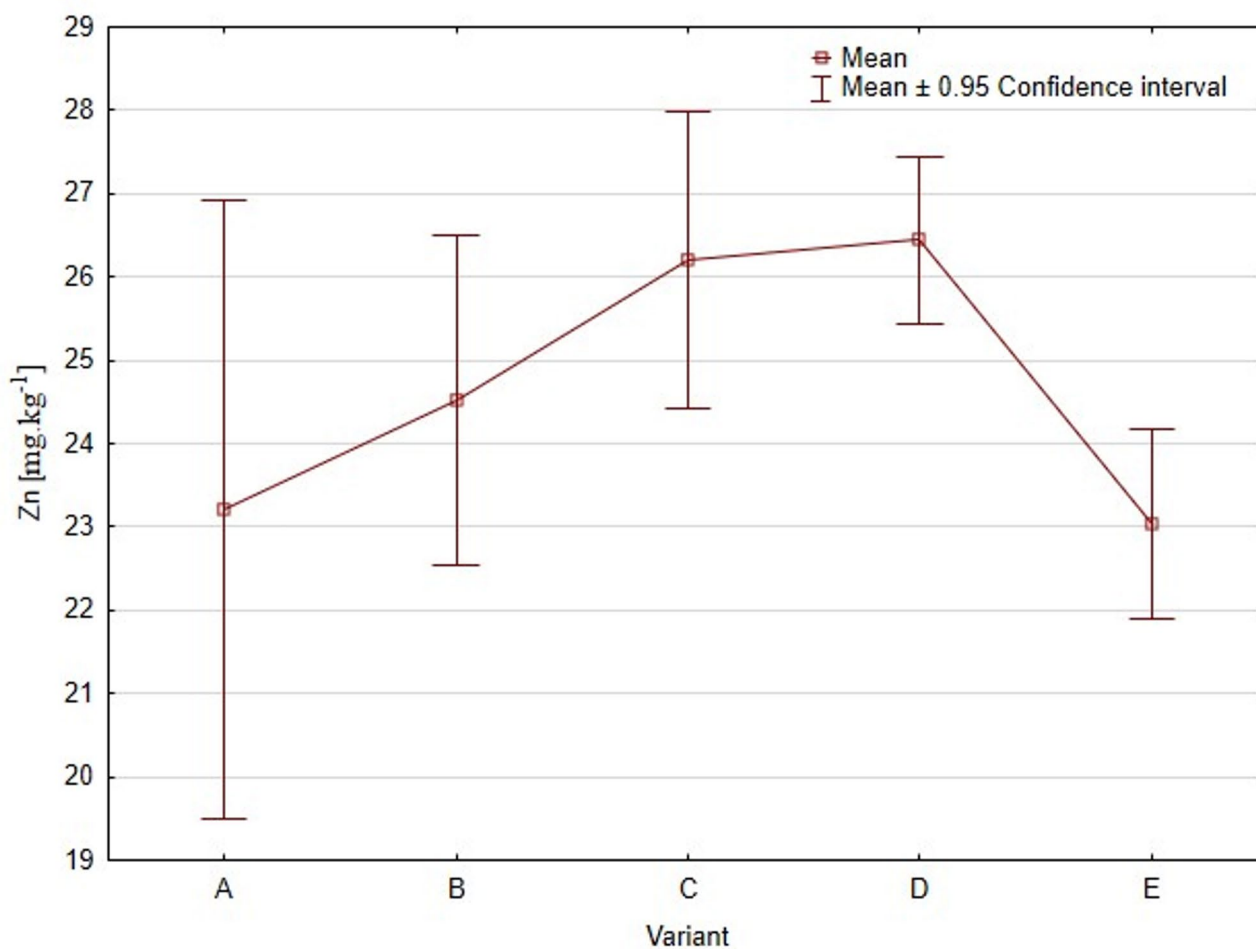


Fig. 9. Average content of Zn depending on variants. Variants of soil modifications A – NPK; B – Mo; C – Sr; D – As; E – Cd.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	4.13	17.34	1.01	1.46	-23.57	18	0.000
A vs. C	10	10	4.13	11.89	1.01	0.76	-19.41	18	0.000
A vs. D	10	10	4.13	5.01	1.01	4.30	-0.63	18	0.537
A vs. E	10	10	4.10	2.67	1.01	0.75	3.67	18	0.002

Table 8. Comparison of the significance of differences in average concentration of mo depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	28.74	29.09	1.06	1.155	-0.706	18	0.489
A vs. C	10	10	28.74	28.35	1.06	2.251	0.496	18	0.626
A vs. D	10	10	28.74	26.67	1.06	3.422	1.828	18	0.084
A vs. E	10	10	28.74	26.54	1.06	1.366	4.026	18	0.001

Table 9. Comparison of the significance of differences in average concentration of Mn depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	1.240	1.360	0.515	0.425	-0.569	18	0.577
A vs. C	10	10	1.240	8.83	0.515	1.480	-15.322	18	0.000
A vs. D	10	10	1.240	1.840	0.515	0.386	-2.948	18	0.009
A vs. E	10	10	1.240	2.050	0.515	0.687	-2.985	18	0.008

Table 10. Comparison of the significance of differences in average concentration of Sr depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	1.47	1.12	0.585	0.20	1.79	18	0.090
A vs. C	10	10	1.47	1.34	0.585	0.50	0.55	18	0.592
A vs. D	10	10	1.47	1.43	0.585	0.46	0.17	18	0.867
A vs. E	10	10	1.47	1.47	0.585	0.51	0.00	18	1.000

Table 11. Comparison of the significance of differences in average concentration of cr depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	0.31	0.29	0.062	0.024	1.05	18	0.307
A vs. C	10	10	0.31	0.29	0.062	0.041	0.73	18	0.478
A vs. D	10	10	0.31	2.48	0.062	0.405	-16.75	18	0.000
A vs. E	10	10	0.31	0.25	0.062	0.041	2.83	18	0.011

Table 12. Comparison of the significance of differences in average concentration of as depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	0.41	0.38	0.06	0.05	1.37	18	0.188
A vs. C	10	10	0.41	0.44	0.06	0.08	-0.85	18	0.406
A vs. D	10	10	0.41	0.33	0.06	0.07	2.58	18	0.019
A vs. E	10	10	0.41	4.43	0.06	0.73	-17.46	18	0.000

Table 13. Comparison of the significance of differences in average concentration of as depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	0.48	0.37	0.13	0.06	2.28	18	0.035
A vs. C	10	10	0.48	0.37	0.13	0.08	2.29	18	0.034
A vs. D	10	10	0.48	0.34	0.13	0.07	2.80	18	0.012
A vs. E	10	10	0.48	0.39	0.13	0.07	1.77	18	0.094

Table 14. Comparison of the significance of differences in average concentration of Pb depending on variants.

Although the addition of cadmium did increase its content in the grain of spring barley (*Hordeum vulgare* L.), the BCF value was lower than in the uncontaminated variant, which may indicate the presence of a natural biological barrier in plants that limits the transport of such elements into generative organs. Cadmium accumulation in *Hordeum vulgare* L. in a simulated experiment was also observed by Haddad et al.⁴⁹ who

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	2.90	2.19	0.58	0.46	3.02	18	0.007
A vs. C	10	10	2.90	2.52	0.58	0.42	1.67	18	0.113
A vs. D	10	10	2.90	2.50	0.58	0.56	1.56	18	0.136
A vs. E	10	10	2.90	2.36	0.58	0.86	1.64	18	0.118

Table 15. Comparison of the significance of differences in average concentration of Cu depending on variants.

Variants	N [-]		Mean [mg.kg ⁻¹]		St. dev. [mg.kg ⁻¹]		t-test [-]	df [-]	p-level [-]
	A	B	A	B	A	B			
A vs. B	10	10	23.20	24.53	5.19	2.77	-0.72	18	0.484
A vs. C	10	10	23.20	26.210	5.19	2.49	-1.65	18	0.115
A vs. D	10	10	23.20	26.440	5.19	1.40	-1.91	18	0.073
A vs. E	10	10	23.20	23.040	5.19	1.59	0.09	18	0.927

Table 16. Comparison of the significance of differences in average concentration of Zn depending on variants.

Element X vs. element Y	Variant	N	Mean	Standard deviation (SD)	t	p	r(X, Y)	Intercept	Slope
Mo - Mn	C	10	28.35	2.25	2.97	0.018	0.72	2.88	2.14
Mo - Zn	A	10	23.20	5.19	-2.50	0.037	-0.66	37.24	-3.40
As - Mn	E	10	26.54	1.37	3.00	0.017	0.73	20.55	24.44
As - Zn	B	10	24.53	2.77	-3.02	0.017	-0.73	48.66	-83.50
Mo - Pb	A	10	0.48	0.13	2.32	0.049	0.63	0.14	0.08
Mo - Pb	E	10	0.39	0.07	-2.36	0.046	-0.64	0.56	-0.06
Cr - Sr	D	10	1.84	0.39	2.96	0.018	0.72	0.98	0.60
As - Mo	B	10	17.34	1.46	2.36	0.046	0.64	6.23	38.45

Table 17. Results of regression and correlation analysis of selected elements.

concluded that, in general, heavy metal accumulation was higher in roots compared to vegetative parts. Their findings are also supported by the work of Sekara et al.⁶² as well as González, and Lobo⁶³.

When evaluating the concentration of Pb in barley grains, statistically significant differences in average concentrations were found out among variant A and variants B, C, and D. When comparing variants A and E, statistically significant differences in average concentrations of Pb were observed at the significance level of 10%. In all cases (with the addition of Mo, Sr, As, and Cd), an antagonistic effect on Pb concentration was observed compared to the control. McBride in their study⁴² assessed the effectiveness of soil modifications to reduce the transfer of Pb and As to leafy green vegetables from historically contaminated soils. A low degree of correlation between Pb and As intake from soil contaminated with both selected elements was found out in their study. Liu et al. focused on studying cultivar variation in the accumulation and distribution of cadmium and lead among 30 wheat cultivars (*Triticum aestivum* L.)⁴³. Based on this study, an antagonistic interaction between Cd and Pb in accumulation in wheat roots and shoots was confirmed, which will be further studied in field experiments.

By evaluating the average copper concentrations in individual variants, only one case of differences in the level of statistical significance was found. The addition of Mo caused a statistically significant decrease in the average concentration of Cu in barley grains. Shi et al. conducted a potted culture experiment to study the effects of *Claroideoglomus etunicatum* BEG 168 vaccination on growth and Mo content in maize growing in soil supplemented with different levels (0; 1,000; 2,000; 4,000 mg.kg⁻¹)⁴⁴. Based on this study, the addition of Mo reduced the dry weight of the plants and the content of leaf pigment, as well as the intake of Cu in shoots and roots.

The last monitored selected elements was zinc. A statistically significant difference in the average concentration of this selected elements was monitored when comparing variant A with variant D. Soil modification with the addition of As caused a statistically significant increase in the average concentration of Zn. According to a previous study³⁷ the toxicity of arsenic reduced the concentrations of Zn.

Correlation of a pair of selected elements

Based on our analysis at the unit change of Mo, Mn in barley grains increased by an average of 2.14 mg.kg⁻¹ when grown in strontium-enriched soil. According to a study⁶⁴ there was little evidence of antagonistic action

between Mo and Mn. In oats, the intake of one element was independent of the amount of the other present element. In our case, the positive correlation could be caused by the addition of Sr, which may be evidence of a change in the bioavailability of selected elements with different additions of other elements to the soil.

By statistical analysis, we found out that with a unit change in Mo, Zn decreases on average by 3.4 mg.kg^{-1} if the soil is not enriched with any selected elements (variant NPK-A). Basak et al.⁶⁵ investigated the interaction between the additions of Mo and other elements in the plant parts of rice. According to this study, increasing doses of applied Mo tended to decrease the concentration of Zn in both shoots and roots. These results are consistent with our results. Singh and Steenberg investigated micronutrient interactions in barley grown on zinc-contaminated soils. According to this study⁶⁶ the concentration of Mo showed a slight tendency to decrease with increasing rate of added Zn, but the results were not consistent in the roots and tops of the barley in any of the soils. The results of this study correspond to our findings.

According to a study by Basak et al.⁶⁷ the application of Mo at a higher value increased the content of extractable Zn in the soil. However, this experiment was conducted in waterlogged rice soil, which could have an impact on a different interaction of the two elements. According to our study, barley grain with a unit change of As increases on average the Mn content by 24.44 mg.kg^{-1} with the addition of Cd. Shaibur et al. demonstrated that the concentration and accumulation of Mn decreased significantly in barley shoots with the addition of As compared to shoots without the addition of As⁶⁸. The opposite correlation between As and Mn in our case could be caused by the addition of Cd to the soil.

According to our results, the addition of Mo to the soil caused an average reduction in Zn at the unit change of As by 3.4 mg.kg^{-1} . According to a study⁶⁸ the accumulation of Zn in barley roots decreased with the addition of As. Our results are consistent with a negative correlation between As and Zn compared to the study cited. A correlation was also found out between the content of Mo and Pb in barley grains. In the variant without the addition of selected elements (Variant A – NPK), it was determined that at the unit change of Mo, Pb increased by an average of 0.08 mg.kg^{-1} without the addition of selected elements. On the contrary, with the addition of Cd to the soil, it was found out that with a unit change of Mo, Pb decreases by an average of 0.06 mg.kg^{-1} . In a comparative study, a slightly negative correlation between Mo and Pb in barley grains (-0.01) was confirmed⁶⁹.

Statistical evaluation of our results confirmed that with a unit change in Cr, Sr increases on average by 0.6 mg.kg^{-1} with the addition of As. Likewise, an average increase in Mo of 38.45 mg.kg^{-1} at the unit change of As (addition of Mo) was confirmed.

The mutual correlations between individual heavy metals in terms of their bioavailability to plants represent an interesting topic. A multivariate statistical analysis of heavy metal bioavailability in selected coastal flora species was conducted in a study by Chudasama et al.⁷⁰. These authors examined the inter-element correlations of Cu, Fe, Mn, and Zn in plant species naturally growing along the coast of the Indian Ocean⁷⁰. While we also assessed the concentrations of Mn, Zn, and Cu, the most significant impacts in our study likely resulted from the simulated addition of elements such as Mo, Sr, As, and Cd. The model of sorption of Cu, Zn, Cd, Mn from sewage sludge as well as their chemistry was also discussed by Samešová et al.⁷¹ and Ďuricová et al.⁷².

More relevant to our results appears to be the study by⁶¹ who analyzed the content of copper, zinc, cadmium, and lead in soil used for pot cultivation, as well as in the roots and leaves of all sampled plant species. Based on these data, bioconcentration and translocation factors were calculated to evaluate the bioaccumulation potential of the studied species. Within the Poaceae family, they focused on the autochthonous species *Lolium multiflorum* L. Bioconcentration factors (BCF) for lead were slightly higher than those observed in our studied spring barley, while those for cadmium and zinc were comparable, and for copper, they were lower. These differences, however, may be attributed to species-specific traits and a complex set of soil-ecological factors.

Conclusion

By statistical evaluation in our study, we found out that the addition of Mo (variant B) and Sr (variant C) led to a statistically significant increase in molybdenum content in barley grains compared to soil modification with the addition of NPK (without the addition of other selected elements). With the addition of Cd, a significant reduction in molybdenum content in barley grains was noted compared to soil amendment without the addition of selected elements (variant A – NPK). The addition of As resulted in a statistically significant reduction in the average concentration of manganese content at the 10% significance level of the test ($p=0.084$). When monitoring the chromium content and when comparing variant A with other variants, a statistically significant difference in Cr concentrations was found out only in the case of the A–B variant. A statistically significant reduction in cadmium concentration at the 5% significance level of the test was caused by the addition of arsenic in variant D. It was found out that the addition of Sr led to a statistically significant increase in molybdenum content compared to control NPK sample. The addition of Cd caused a statistically significant reduction in Mn content compared to soil modification with NPK. Using the T-test, a positive relationship between Mo and Mn was confirmed for the addition of Sr, As and Mn for the addition of Cd; Cr and Sr with the addition of As.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

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Author contributions

All authors contributed to the study conception and design. Study conception and design were performed by M. S. Material preparation and data collection were performed by K. K., D. S. and P. A. Analysis were performed by J. S. and J. P. The first draft of the manuscript was written by D. V. and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare no competing interests.

Additional information

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